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Isotachophoretic separation of rare earth ions I. Separation behaviour of yttrium and fourteen lanthanide ions forming complexes with tartaric acid and α-hydroxyisobutyric acid

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Abstract

A leading electrolyte for the isotachophoretic separation of yttrium ion from lanthanide ions was developed, consisting of 20 m*M* ammonia solution containing 0.5 m*M* tartaric acid and 8 m*M* α-hydroxyisobutyric acid (HIB) as complex-forming agents. The pH of the solution was adjusted to 4.8 by adding acetic acid. Using the electrolyte system developed, the separation behaviour of fifteen rare earth ions was studied in comparison with a simple HIB system. It was revealed that the addition of tartaric acid lowered the separability of adjacent pairs of medium and heavy lanthanide ions to two-thirds of that of HIB system, instead of the successful separation of Dy and Y. The electrolyte system developed was applied to the separation of a rare earth ore sample containing Y as one of the major components.

1. Introduction

The fourteen lanthanide cations can be separated by isotachophoresis (ITP) by using a leading electrolyte containing a complexing agent, α-hydroxyisobutyric acid (HIB) [1,2]. A typical leading electrolyte is 20 m*M* ammonia solution containing 10 m*M* HIB buffered to pH 4.8 by adding acetic acid, which is used in combination with a suitable terminating electrolyte, e.g., 10 m*M* carnitine hydrochloride solution. By using the above operational electrolyte system, referred to hereafter as the HIB system, the lanthanide cations can be separated in order of increasing atomic number. The separability between the adjacent pairs of lanthanide ions is not constant but varies periodically, forming four different subgroups (tetrad effect [3]) from 27 nmol/C (Eu–Gd pair) to 309 nmol C^{-1} (Gd–Tb pair) [4].

The HIB system can be successfully applied to the analysis of rare earth ores such as monazite, of which light lanthanides are the major component [5]. However, when the HIB system was applied to different rare earth ores containing significant amounts of Y^{3+}, a problem arose in that Y^{3+} and Dy^{3+} could not be separated to form a mixed zone and accurate analysis was

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impossible. As rare earth ores such as ion-adsorption-type ore and Xenotime ore contain Y^{3+} and Dy^{3+} with considerable abundances, another operational electrolyte system is necessary to permit the isotachophoretic separation of these two elements. The low separability of Y^{3+} and Dy^{3+} is due to the similarity of the absolute mobilities and stability constants of their HIB complexes [6]. Effective separation of these cations is therefore impossible when HIB alone is used as a complexing agent.

Recently, we have studied the isotachophoretic separation behaviour of twenty kinds of metal ions, including La^{3+}, Ce^{3+}, Gd^{3+}, Lu^{3+} and Y^{3+}, using leading electrolytes containing tartaric acid as the complex-forming agent [7]. The separation behaviour of the four lanthanide ions and Y^{3+} in the above electrolyte system was different from that of the HIB system. That is, the decreases in the effective mobilities of Gd^{3+} and Lu^{3+} with respect to tartaric acid concentration were very similar to each other, but the decrease was different from that of Y^{3+}. This suggested the possible separation of Y^{3+} from lanthanide ions by adding tartaric acid to the HIB system as another complex-forming agent.

The aim of this study was to develop an operational electrolyte system suitable for the separation of Y^{3+} from lanthanide ions and to demonstrate the utility of the electrolyte system in the analysis of a real rare earth ore containing both types of ions.

2. Experimental

2.1. Samples

An equimolar mixture containing Tb^{3+}, Dy^{3+} and Y^{3+} (1.67 m*M*) was used to optimize the tartaric acid concentration in the leading electrolyte. Another equimolar mixture of fifteen rare earth ions (Y^{3+} and the fourteen lanthanide ions: La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+} and Lu^{3+}) was used to assess the separability of the electrolyte system developed. The concentration of each component was 0.33 m*M*. These test mixtures were prepared from stock solutions of the chlorides (5 m*M*), which were prepared by dissolving the compounds in purified water.

A 2 g l^{-1} solution of an ion-adsorption-type rare earth ore was prepared as follows: 0.5 g of the ore powder was dissolved in a PFTE vessel by adding 5 ml of concentrated hydrochloric acid, then evaporated to dryness by using a 500 W lamp to remove excess hydrochloric acid. Subsequently, 5 ml of water were added and the mixture was evaporated to dryness again. Finally, the chloride residue was dissolved in deionized water to 250 ml. The pH of the sample solution prepared was 2.6.

2.2. Operational electrolyte system

The operational electrolyte systems used are summarized in Table 1. The leading electrolytes containing different concentration of tartaric acid and HIB were prepared by mixing two leading electrolytes: 20 m*M* ammonia solution containing 10 m*M* HIB and 20 m*M* ammonia solution containing 2.5 m*M* tartaric acid. The pH of both solutions was adjusted to 4.80 by adding acetic acid. The terminating electrolyte was a 10 m*M* solution of carnitine hydrochloride. All the electrolytes contained 0.1 mass-% hydroxypropylcellulose (HPC) to suppress electroendosmosis. The electrolyte systems containing both HIB and tartaric acid as complexing agents are referred as the HIB–Tar system. A Horiba (Tokyo, Japan) Model F7-AD expanded pH meter was used for pH measurements.

2.3. Chemicals

The rare earth chlorides were of guaranteed grade (GR) from Katayama Chemical (Osaka, Japan). Powdered ion-adsorption-type rare earth ore (a mixture of rare earth oxides) was obtained from Nippon Kogyo (Tokyo, Japan). Hydrochloric acid was of ultrapure grade from Merck (Darmstadt, Germany). The complexing agents α-hydroxyisobutyric acid (GR) and tartaric acids (GR) and HPC (extra pure) were obtained from Tokyo Kasei (Tokyo, Japan). The viscosity of a

Table 1
Operational electrolyte system for isotachophoresis

Leading electrolyte	20 m*M* NH_3 solution
Complexing agent	(1) 10 m*M* α-hydroxyisobutyric acid (HIB)
	(2) 8.4 m*M* HIB, 0.4 m*M* tartaric acid
	(3) 8.0 m*M* HIB, 0.5 m*M* tartaric acid
	(4) 7.6 m*M* HIB, 0.6 m*M* tartaric acid
	(5) 7.2 m*M* HIB, 0.7 m*M* tartaric acid
	(6) 5.0 m*M* HIB, 1.25 m*M* tartaric acid
pH buffer	Acetic acid
pH	4.80
Additive	0.1 mass-% hydroxypropylcellulose
Terminating electrolyte	10 m*M* carnitine hydrochloride
Additive	0.1 mass-% hydroxypropylcellulose

2% (w/w) HPC aqueous solution was 1000–4000 cP at 20°C according to the specification.

2.4. Isotachophoretic apparatus and R_E measurement

The detector for ITP was a high-frequency contactless conductivity detector (HFCCD) [8], which was used in combination with the separation unit of a Labeco (Sp. Nova Ves, Slovakia) ZKI-001 isotachophoretic analyser. The separation column used consisted of a preseparation capillary (10 cm × 0.5 mm I.D. or 20 cm × 0.5 mm I.D.) and a main capillary (20 cm × 0.25 mm I.D.). The migration current in the preseparation stage was 125 μA and it was decreased to 50 μA while detecting zones. When the short preseparation tube was used, the amount of electric charge applied until the detection of the terminating zone was 0.27 C in the blank run, and 0.37 C for the long run. The high-voltage power supply was that for a Shimadzu (Kyoto, Japan) IP-2A system. Measurements were carried out at 25°C in a temperature-controlled room.

The qualitative index used was R_E, defined as the ratio of the potential gradient [E(Vcm^{-1})] of the sample zones (E_S) to that of the leading zone (E_L) [9]. When a conductivity detector is used, it is equal to the ratio of specific resistance (ρ) of each zone. As the output signal of the HFCCD showed a non-linear response to the specific resistance of the zones [8], the signal obtained was converted into the specific resistance using a fourth-order polynomial expression of the output voltage. The expression was obtained using KCl solutions with known specific resistance. Na^+ and Li^+ were used as the internal standard to correct slight drift of the HFCCD signals. The simulated R_E values were 1.495 and 1.963, respectively.

3. Results and discussion

3.1. Separation of Y^{3+} from lanthanide ions

To optimize the tartaric acid concentration in the leading zone for the separation of Y^{3+} from lanthanide ions, the separability of an equimolar test mixture of Tb^{3+}, Y^{3+} and Dy^{3+} was examined using six leading electrolytes as shown in Table 1. It should be noted that the concentration of both tartaric acid and HIB in the electrolytes were different with each other.

Fig. 1 shows the isotachopherograms obtained for the test mixture (sample amount = 1.67 nmol × 3). It is obvious that the separability among the above ions depended sensitively on the tartaric acid concentration. When the tartaric acid concentration (C_{Tar}) was 0.5 m*M* (Fig. 1b) and 0.6 m*M* (Fig. 1c), Tb^{3+}, Y^{3+} and Dy^{3+} were separated in that order. However, the separation was impossible, when C_{Tar} was 0.4 and 0.7 m*M* (Fig. 1d). The HIB concentration (C_{HIB}) in the leading electrolyte was 8, 7.6, 8.4 and 7.2 m*M*, respectively.

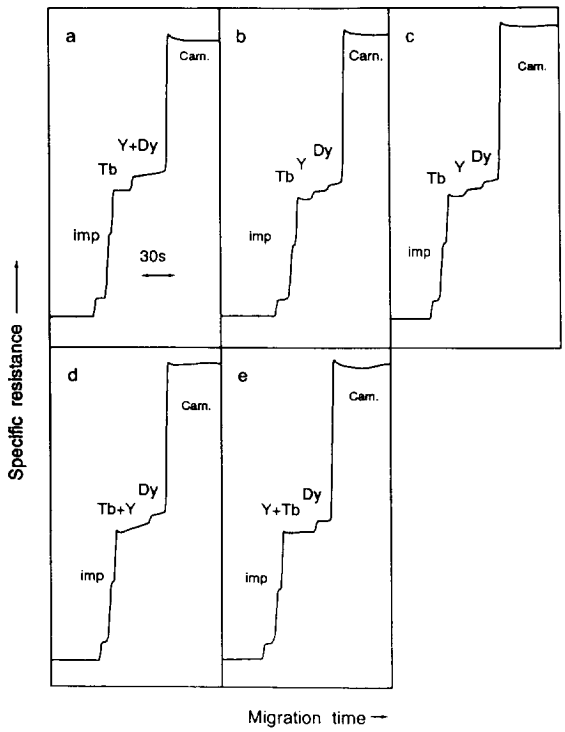

Fig. 1. Isotachopherograms of an equimolar mixture of Tb^{3+}, Y^{3+} and D^{3+} (1.67 m*M* 1 μl) obtained by using five leading electrolytes containing different concentrations of tartaric acid and HIB. Imp = electrolyte impurity. Migration current 50 μA. See Table 1 for details of the electrolyte systems used. C_{Tar} = (a) 0; (b) 0.5; (c) 0.6; (d) 0.7; (e) 1.25 m*M*.

Next the separation efficiency (nmol C^{-1}) of six rare earth ions (Eu^{3+}, Gd^{3+}, Tb^{3+}, Y^{3+}, Dy^{3+} and Ho^{3+} in order of migration) was measured for adjacent pairs by using the method reported previously [4]. The results are summarized in Table 2 together with the values observed for the HIB system [4]. Obviously from Table 2, the separation efficiency of the HIB–Tar system was ca. two-thirds of that of the HIB system. The separation efficiency of the Tb–Y and Y–Dy pairs was especially sensitive to the tartaric acid concentration because of the small effective mobility difference. In the analysis of real samples, therefore, the tartaric acid concentration should be optimized considering the abundance of Tb, Y and Dy. The separation of Tb, Y and Dy was thus achieved by using the HIB–Tar system, but the addition of tartaric acid decreased the separability of adjacent pairs of medium and heavy lanthanide ions.

Table 2
Separation efficiency observed for equimolar binary mixtures of adjacent lanthanide ions

Ions	Separation efficiency (nmol C^{-1})[a]		
	HIB[b]	HIB–Tar	
		C_{Tar} = 0.5 m*M*	C_{Tar} = 0.6 m*M*
Eu–Gd	27	0	0
Gd–Tb	309	220	166
Tb–Y		10	35
Tb–Dy	245	166	158
Y–Dy		100	75
Dy–Ho	197	137	112
Ce–Pr	180	166	176

The electrolyte systems were as in Table 1.
[a] Total amount of the separands/applied charge. Accuracy is ±5 nmol C^{-1}.
[b] Observed values for the HIB system [4].

3.2. Separation behaviour of rare earth ions

Fig. 2 shows the isotachopherograms of an equimolar mixture of the fifteen rare earth ions obtained by using three different leading electrolytes. When the HIB system was used, as shown in Fig. 2a, Y^{3+} and Dy^{3+} had the same step height. Although the same step height of separands at the isotachophoretic steady state does not always mean an imperfect separation [7], ITP–PIXE (particle-induced X-ray emission) analysis revealed that most of Y^{3+} and Dy^{3+} formed a mixed zone. The composition of the zone front suggested the effective mobility of Y^{3+} was slightly larger than that of Dy^{3+} [4].

When the HIB–Tar system (C_{Tar} = 0.5–0.6 m*M*) was used, Y^{3+} and Dy^{3+} were separated as expected (Fig. 2b). However, the Eu^{3+} and Gd^{3+} zones had the same step height, and the zone was also a true mixed zone according to ITP–PIXE analysis. The low separability of Eu^{3+} and Gd^{3+} is mainly caused by the fact that the stability constants of $Eu(AcO)_n^{3-n}$ complexes are larger than those of $Gd(AcO)_n^{3-n}$ complexes

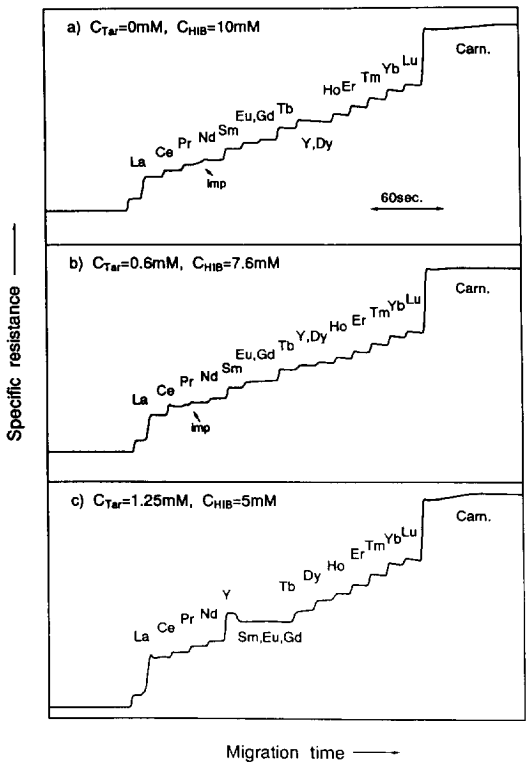

Fig. 2. Isotachopherograms of an equimolar mixture of fifteen rare earth ions (0.33 m*M*, 5 μl) obtained by using three different leading electrolytes. Electrolyte systems as in Table 1. Imp = electrolyte impurity. Migration current 50 μA.

[10], contrary to the HIB case. It seems that the stability constants of Eu–tartrate complexes are larger than those of Gd–tartrate complexes, similarly to the acetate complexes. When the tartaric concentration was increased and the HIB concentration was decreased, as shown in Fig. 2c, the Y^{3+} zone migrated before the Sm^{3+}, Eu^{3+} and Gd^{3+} mixed zone in an enforced manner [11]. The separability decrease on addition of tartaric acid was not observed for light lanthanide ions, as shown in Table 2 for Ce and Pr.

Table 3 shows the R_E values of the fifteen rare earth ions observed for the HIB system and the HIB–Tar system (C_{Tar} = 0, 0.4, 0.5, 0.6 and 0.7 m*M*). The effective mobilities of the rare earth ions were given as $\bar{m}_L/R_E$ from the definition of R_E, where $\bar{m}_L = 72.5 \cdot 10^{-5}$ cm^2 V^{-1} s^{-1} according to our simulation. Clearly from Table 3, the R_E values of rare earth ions increased slightly on adding tartaric acid, in spite of the decrease in HIB concentration. When the concentration was 0.6 m*M*, for example, the effective mobility of Y^{3+} ($20.5 \cdot 10^{-5}$ cm^2 V^{-1} s^{-1}) was between those of Tb^{3+} ($21.1 \cdot 10^{-5}$ cm^2 V^{-1} s^{-1}) and Dy^{3+} ($20.1 \cdot 10^{-5}$ cm^2 V^{-1} s^{-1}) and consequently the separation was achieved. This suggested that the stability constants of Y–tartrate complexes are smaller than those of Dy–tartrate complexes.

Table 3
R_E values of rare earth ions observed by using five leading electrolytes

Rare earth ion	Electrolyte system[a]				
	1	2	3	4	5
C_{Tar} (m*M*)[b]	0	0.4	0.5	0.6	0.7
C_{HIB} (m*M*)[c]	10	8.4	8.0	7.6	7.2
La	2.24	2.33	2.42	2.40	2.43
Ce	2.45	2.54	2.69	2.68	2.71
Pr	2.59	2.72	2.80	2.78	2.81
Nd	2.72	2.80	2.90	2.88	2.91
Sm	3.01	3.09	3.22	3.18	3.21
Eu	3.16	3.25	3.41	3.35	3.37
Gd	3.25	3.29	3.44	3.35	3.37
Tb	3.55	3.57	3.74	3.64	3.72
Y	3.79	3.73	3.90	3.75	3.72
Dy	3.79	3.80	3.98	3.88	3.89
Ho	3.97	3.96	4.15	4.04	4.05
Er	4.19	4.16	4.36	4.25	4.26
Tm	4.42	4.37	4.60	4.47	4.49
Yb	4.66	4.61	4.86	4.72	4.74
Lu	4.83	4.77	5.03	4.87	4.90
T[d]	5.65	5.85	5.94	6.17	5.98

[a] Electrolyte numbers as in Table 1.
[b] C_{Tar} = total concentration of tartaric acid.
[c] C_{HIB} = total concentration of α-hydroxyisobutyric acid.
[d] Terminating zone.

As it was expected that better resolution might be obtained by increasing the HIB concentration, a leading electrolyte containing 10 m*M* HIB and 0.5 m*M* tartaric acid was applied to the rare earth elements. Although the separation of Eu and Gd was slightly improved, no clear steps were observed between the zones. When the HIB concentration was increased to 11 m*M*, the recovery of Lu began to decrease. It was less than 50% when the concentration was 12 m*M*.

This might be explained by the effective mobility of Lu at the transient state being smaller than that of the terminator (H^+) when the HIB concentration was higher than 10 m*M*.

3.3. Analysis of an ion-adsorption-type ore

An ion-adsorption-type ore containing a considerable amount of Y was analysed by using the HIB–Tar operational electrolyte system. Fig. 3 shows the isotachopherograms of the ore sample (2 g l^{-1}) obtained by using three different electrolyte systems [C_{Tar} = (a) 0, (b) 0.6 and (c) 1.25 m*M*. The volume injected was 3 μl. Obviously from Fig. 3a, Y^{3+} and Dy^{3+} merged into a zone when the HIB system was used, but they were separated with the HIB–Tar system (Fig. 3b). C_{Tar} was selected as 0.6 m*M* rather than 0.5 m*M* considering the separability shown in Table 2, because the abundance of Dy in the sample was greater than that of Tb. If Y and Dy are the targets of the analysis, a higher concentration of tartaric acid may be suitable, as shown in Fig. 3c.

The zone passing times of the major components in the rare earth ore sample were measured by varying the sample volume by using the HIB–Tar system and the HIB system to show the differences in separability. The results are shown in Figs. 4 and 5. In addition to the point that Y and Dy can be analysed separately by using HIB–Tar system, it is clear that better separability was obtained for Pr and Nd. Concerning Ce, the coincidence of the step with that of an electrolyte impurity (unidentified) made the zone passing time unstable. When the HIB system was used, a better result was obtained for Ce, as shown in Fig. 5. Figs. 4 and 5 show that the zone passing times per unit amount of sample were almost identical.

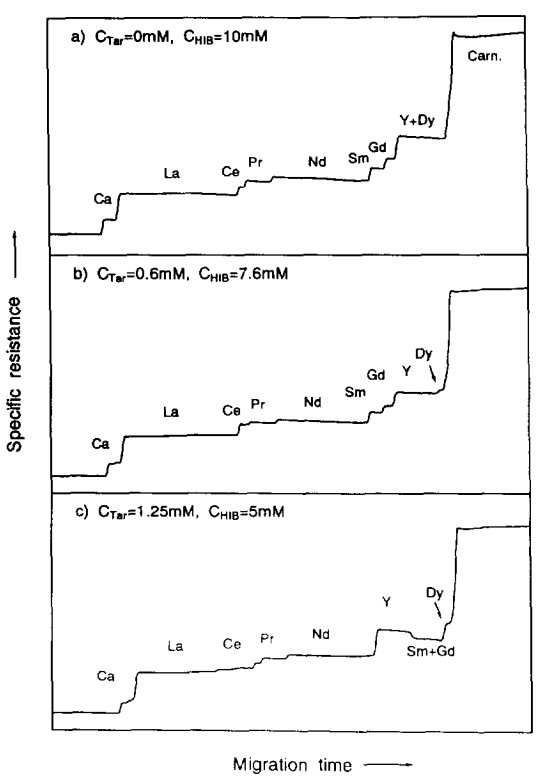

Fig. 3. Isotachopherograms of an ion-adsorption-type rare earth ore (2 g l^{-1}, 3 μl) obtained by using the HIB system and the HIB–Tar system (C_{Tar} = 0.6 and 1.25 m*M*).

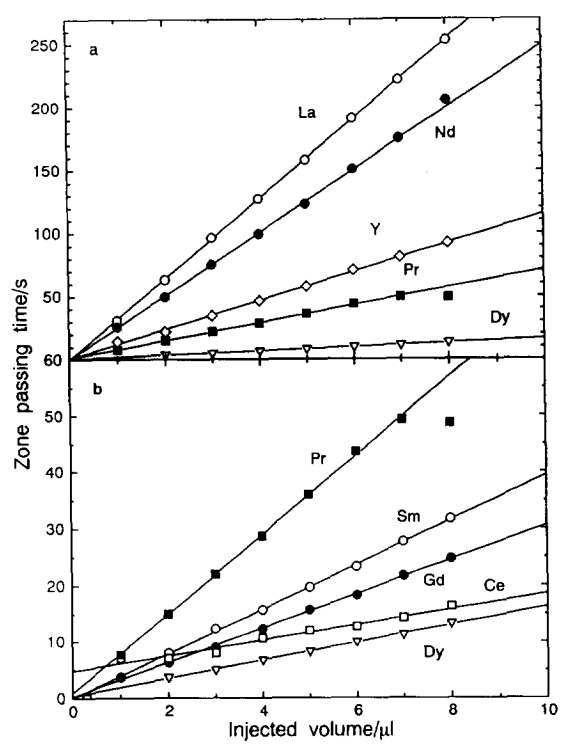

Fig. 4. Zone passing time vs. injection volume for an ion-adsorption-type rare earth ore (2 g l^{-1}) obtained by using the HIB–Tar system. Migration current 50 μA.

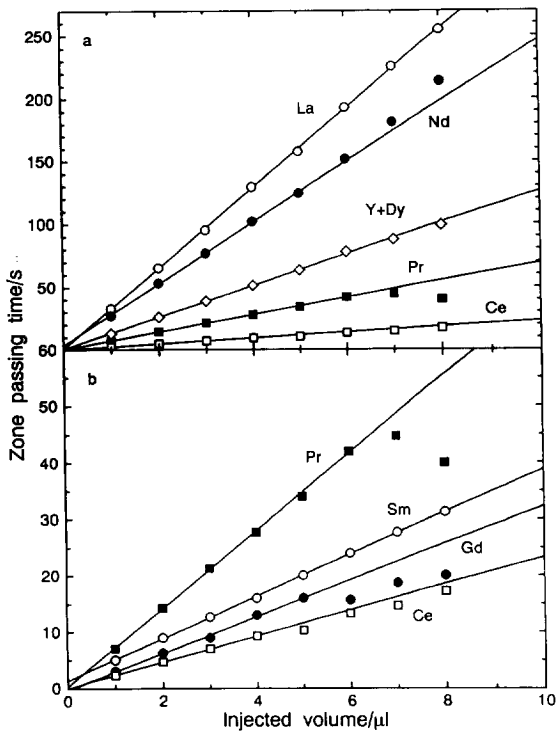

Fig. 5. Zone passing time vs. injection volume of an ion-adsorption-type rare earth ore (2 g l^{-1}) obtained by using the HIB system. Migration current 50 μA.

Table 4 summarizes the analytical results for the ore sample obtained by ITP, together with those given by PIXE and ITP–PIXE. Good agreement was obtained for the major components. Accurate results were obtained by ITP even for the minor components such as Ce and Dy, the abundances of which were 2 mass-%. ITP appears to be the most convenient method for determining rare earth elements at such a level of abundance. The elements with abundances of the order of 0.1% (w/w) can be determined by applying much more charge with the use of a longer capillary.

It is very convenient if the fifteen rare earth ions (lanthanide and yttrium ions) can be separated simultaneously using one electrolyte system. However, such a separation is impossible at present. The two electrolyte systems described in this paper are necessary for the analysis. In addition, Sc^{3+} was not treated in this study, as it has high stability constants even with acetate ions and it could not be detected as cations in ITP.

The capillary zone electrophoretic separation of lanthanides was reported by Foret et al. [12]. We modified the reported electrolyte system (30

Table 4
Analytical results for an ion-adsorption-type rare earth ore

Rare earth ion	ITP [10 μl (2 g l^{-1})]		ITP–PIXE [14 μl (2 g l^{-1})]		PIXE [5 μl (0.8 g l^{-1})]	
	μg	Mass-%[a]	μg	Mass-%[a]	μg	Mass-%[a]
La	5.539	36.68	7.425	35.96	1.020	35.22
Ce	0.300	1.98	0.431	2.09	0.083	2.87
Pr	1.211	8.02	1.747	8.46	0.260	8.98
Nd	4.725	31.29	6.465	31.31	0.860	29.7
Sm	0.710	4.70	1.001	4.85	0.135	4.66
Eu	–		0.145	0.70	0.039	1.35
Gd	0.649	4.30	0.674	3.26	0.115	3.97
Tb	–		0.104	0.50	0.035	1.21
Dy	0.302	2.00	0.405	1.96	0.054	1.86
Ho	0.052	0.34	0.073	0.35	0.007	0.2
Er	0.134	0.89	0.164	0.79	0.010	0.35
Tm	–		0.040	0.19	0.008	0.3
Yb	0.131	0.87	0.135	0.65	0.015	0.52
Lu	–		0.021	0.10	0.008	0.3
Y	1.347	8.92	1.820	8.81	0.247	8.53
Total	15.100		20.650		2.896	

[a] Mass-% = mass of a rare earth element/total mass of rare earth elements ×100.

m*M* creatinine–acetate buffer containing 4 m*M* HIB) by adding tartaric acid and applied the modified electrolyte system to the separation of rare-earth elements. However, satisfactory separation was not obtained for Tb, Y and Dy. This may be closely related to the fact that the pH and the ionic strength of the separated zones can be regarded as constant in CZE but they are not constant in ITP.

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